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(54) **Organic amine impregnated activated carbon**

Mit organischen Aminen imprägnierte Aktivkohle

Charbon actif imprégné par une amine organique

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Description

[0001] This invention relates to a breathing gas filter composition comprising activated carbon impregnated with an organic amine compound to improve the performance of the activated carbon against toxic perfluorocarbons, particularly trifluoronitrosomethane (TFNM), and to processes for impregnating activated carbon with organic amine compounds.

[0002] Activated carbon has been used in breathing gas filter canisters of gas masks for the removal of toxic gases both commercially and in military applications. For the removal of specific poisonous gases such as hydrogen cyanide (HCN) and cyanogen chloride (CNCI), activated carbons are used which typically contain certain metals (copper, chromium, and silver) usually in the form of an oxide crystallite. Typically, these adsorbents are known in the trade as ASC Whetlerite carbon or ASC/TEDA if the carbon also contains triethylenediamine, TEDA. The function of these metals or metal compounds is primarily to break down HCN or CNCI by chemical reaction(s) into innocuous gaseous products and/or products which are readily physisorbed or chemisorbed onto the activated carbon.

[0003] Trifluoronitrosomethane (TFNM), is a perfluorocarbon which is blue in colour and has a boiling point of -84°C . Under sunlight (UV irradiation), this gas dimerizes, and loses its intense blue hue to become faintly yellow. TFNM is sufficiently toxic to be a high hazard, even to subjects protected by standard carbon adsorbent filters. The amine-impregnated activated carbon described herein was found to be particularly effective in chemisorption of this type of compound.

[0004] From a methodology viewpoint, there are several ways to apply an organic amine to the surface of activated carbon. One proposal for applying TEDA to the surface of activated carbon is found in US patent No. 4,531,953, which was issued to J.E. Groose et al on July 30, 1985. The Groose patent proposes the direct sublimation of TEDA onto the activated carbon surface at atmospheric pressure. Such a process eliminates the subsequent drying procedure because no solvent is involved. Another method for applying TEDA onto the surface of activated carbon under reduced pressure has been detailed in US patent No. 5,145,820, which was issued to S.H. Liang et al on September 8, 1992.

[0005] It is an aim of the invention to provide an organic amine impregnated activated carbon, by which toxic perfluorocarbons, particularly TFNM, can be effectively removed from the breathing air stream, and having an enhanced shelf and service life.

[0006] In one aspect the invention resides in a breathing gas filter composition providing protection against toxic perfluorocarbons, comprising substantially dry activated carbon and an organic amine impregnant in an amount of 1.5 to 18% by weight, based on the weight of the carbon, characterised in that the composition additionally comprises 0.1 to 10% by weight, based on the weight of the carbon, of an alkaline hydroxide.

[0007] In a second aspect the invention resides in a process for impregnating activated carbon by placing a low vapour pressure organic amine in contact with substantially dry activated carbon, characterised by the steps of subjecting the carbon and amine to positive pressure of 1-5 Pa in an oxygen-free inert gas atmosphere and then heating the carbon and amine for an extended period while maintaining the positive pressure of 1-5 Pa in an oxygen-free inert gas atmosphere, and pre-treating the activated carbon with a compound selected from the group consisting of an alkaline hydroxide in an amount of 0.1 to 10% by weight, based on the weight of the carbon, a suitable halogen and a suitable halide salt. The aforesaid heating step may typically be effected at 40° to 60°C , for a period of 1 to 72 hours, depending on the amine impregnant, and the oxygen-free inert gas may be nitrogen, helium, argon etc.

[0008] In a further aspect the invention resides in a process for impregnating activated carbon with a solid amine compound, comprising dissolving the amine in a solvent selected from water and organic solvents and adding the amine solution to the activated carbon characterised by the step of pre-treating the activated carbon with a compound selected from the group consisting of an alkaline hydroxide in an amount of 0.1 to 10% by weight, based on the weight of carbon, a suitable halogen and a suitable halide salt.

[0009] In some known amine impregnated activated carbons, the amines have a tendency to break down (dissociate) due to the presence of acidic surface sites. In the present invention the activated carbon is pretreated to prevent the degradation of the amine compounds on the carbon surface. The pre-treatment procedure can include neutralization to a substantially neutral pH (by an alkaline solution such as KOH or NaOH), or alkalinization to a basic pH in the same manner, or reaction of the acid sites (typically these are oxygen-containing moieties) by halogenation (such as by Cl_2 and Br_2). These treatments effectively de-activate the surface acidic groups on the carbon, thus enhancing the stability of the adsorbed amines on the carbon surface. A US patent No. 4,072,479 issued to Sinha et al on February 7, 1978 has detailed the use of NaOH in the treatment of activated carbon for the removal of malodorous compounds, particularly sulfur-containing compounds from air stream. However, in the present invention the treatment with NaOH is not paramount nor necessary in the protection against perfluorocarbons. Our pretreatment of carbon with NaOH or KOH is used solely to enhance the shelf and service life of the amine-impregnated carbon, particularly in the presence of humid air.

[0010] The use of the process according to the second aspect of the invention facilitates the vaporization of the amine, the penetration of the amine molecules into the micropores on the activated carbon surface, and subsequently the adsorption of the amine molecules onto the activated carbon surface. Furthermore, the inert environment will impede

the oxidation of the amine impregnants on the carbon surface as discussed by Hershman et al, in the US patent No. 4,264,776 issued on April 28, 1981. The lengthy heating step, preferably conducted with continuous mixing in a closed container, allows a "surface distillation" of the amine (by adsorption-desorption processes), thus promoting an even distribution of amine molecules on the activated carbon surface.

5 [0011] The use of substantially dry activated carbon was deemed necessary after testing the impregnation method using two types of activated carbon. The first type was freshly prepared impregnated ASC Whetlerite activated carbon. Since ASC activated carbon must be dried after whetlerization, the drying procedure can be incorporated into the impregnation procedure. The other type of activated carbon was aged activated carbon at various levels of moisture content. For impregnation of amine in the presence of moisture/humid air, the amine molecules have to displace
10 adsorbed water from the activated carbon in order to penetrate into the large surface area available in the meso and micropores. If the micropores on the activated carbon surface are completely or partially filled with water, the adsorption of amine will be limited by how quickly adsorbed water can be displaced which is a kinetic problem. It is also possible that reactions may occur with some of the amines disclosed, if water is present. Therefore, the activated carbon should be dried before the introduction of the amine.

15 [0012] The impregnation step involves the following series of processes:

- (i) sublimation or vaporization of amine;
- (ii) external diffusion of amine molecules to the activated carbon surface;
- (iii) internal diffusion of amine molecules inside the activated carbon pores; and
- 20 (iv) adsorption of amine molecules.

[0013] After impregnating the activated carbon with amine, an equilibration period is provided to allow the amine adsorption process to reach equilibrium. Performing the process at a slightly elevated temperatures of 40°C to 60°C permits repeated desorption and redeposition of the amine to occur. Thus, a more uniform distribution of amine molecules on the activated carbon surface is achieved. In an oxygen-free inert gas environment, the competition for adsorption sites on the carbon surface between the amine and inert gas will be minimal, because inert gas does not adsorb
25 on carbon surface to any appreciable extent. This environment will also enhance the adsorption of amine molecules onto the carbon surface. Furthermore, avoidance of an oxidizing environment inhibits reactions such as the decomposition of tertiary amines in the presence of oxygen and carbon.

30 Brief description of the Drawing:

[0014]

35 Figure 1 is a graph of the breakthrough profile of TFNM on several fresh (i.e. dry) amine-impregnated activated carbons.
Figure 2 is a graph of the breakthrough profile of perfluoroisobutene at 1000 mg/m³ on an activated carbon impregnated with triethylamine.
Figure 3 is a graph of the breakthrough profile of hexafluorocyclobutene at 1000 mg/m³ on an activated carbon
40 impregnated with triethylamine.

Experimental - Chemicals

45 [0015] All amines were purchased from commercial sources and were used without further purification. A wide range of activated carbons have been shown to be suitable for impregnation. Examples given here are ASC whetlerites (i.e. carbons previously impregnated with copper, chromium and silver), ASC/T (ASC Whetlerite, including 2% triethylene-diamine), or a BPL (base carbon with no chemical impregnants).

Pre-treatment of Carbon Halogenation

50 [0016] This reaction can be carried out in either gaseous or aqueous phase. Typically, carbon is stirred in an aqueous Br₂ or Cl₂ solution for several hours (typically 4 to 16 hours). The solution is then removed by suction filtration and the carbon washed with copious amounts of water. The carbon is then dried at 105 to 150°C at reduced pressure (typically < 100Pa). Subsequent to this step, the carbon can be further activated at between 200 to 400°C for up to 4 hours under
55 reduced pressure (typically < 100 Pa).

Neutralization

[0017] A solution containing activated carbon is neutralized to an alkaline pH with an alkaline solution containing an alkaline hydroxide, such as NaOH or KOH. The carbon, including 0.1 to 10% w/w of the alkaline hydroxide, is then washed until a substantially neutral pH is obtained, dried and activated as in the halogenation procedure.

Alkalinization

[0018] Sufficient solution containing 0.1 to 12% (w/w) of the alkaline hydroxide (NaOH or KOH) is added to the activated carbon so that it is visibly saturated. The slurry is then stirred for a minimum of 30 minutes. Heat can be applied to accelerate the process. The solution is then removed by suction filtration, and the carbon dried at 105 to 150°C under reduced pressure (typically <100Pa). Further activation at 200 to 400°C for up to 4 hours may be beneficial for some carbons.

Impregnation of Amines

[0019] Three methods were employed in the impregnation of amine compounds on ASC carbons. The first method (described above) utilizes the inherent (although quite low) vapour pressure of the amines (solid or liquid) to drive the adsorption process. This method works extremely well with all liquid amines and some solid amines e.g. triethylenediamine and hexamethylene-tetramine.

[0020] A second method was designed for solid amides such as ortho- and para-toluenesulfonamide which do not have sufficient vapour pressure for the first method to work. A 250 mL solution containing the desired loading levels (usually 1.5 to 18% by weight) of amide dissolved in 95% ethanol is first obtained. The solution is then added to 250 g ASC charcoal. When the addition of the impregnating solution is completed, the ethanol is removed under reduced pressure from the "wet" carbon. This typically lasts 1/2 to 3/4 hour. By then, the carbon is sufficiently dry and quite free-flowing. The carbon is then spread out uniformly (ca. 0.5 cm high) on two watch glasses and placed inside a vacuum oven. The carbon is dried at less than 100 Pa, 50-60°C for up to 16 hours. Mass balance calculations show that essentially all the ethanol is removed following this treatment, and that all the amide impregnants remain behind, inside the pore structure of the carbon.

[0021] A third method utilizes the solubility in water of the desired impregnants such as urea. The preparation of the solution is very similar to that proposed by Joshua C. Whetzel and E.W. Fuller, who gave rise to the term "Whetlerite". An ammoniacal solution containing about 7% copper, 2% chromium and the desired amide impregnant is prepared. BPL carbon is typically used as a base material in the preparation of these amide-impregnated carbons. The first step of a preparation consists of making an ammonia solution by adding 250 mL of NH_4OH to 400 mL of deionized distilled water. Then 37 grams of CrO_3 , followed by 164 grams of ammonium carbonate, 31 grams of urea and 117 grams of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ is added (in the above order) and dissolved in the solution. This solution is then added onto 440 grams of carbon dropwise until a liquid excess is plainly visible. The ratio of impregnating solution to carbon is approximately 1.4 mL/g. The "wet" impregnated carbon is then removed, drained with occasional shaking for 30 to 40 minutes. The carbon is then spread to an even thickness on a flat container and dried in a forced-draft oven gradually over a period of 220 minutes as follows: 80°C (40 minutes) 100°C (30 minutes), and finally at 120°C (150 minutes). The resulting impregnated carbon typically will have the following composition (w/w): 3% Cr, 10% Cu, 3% urea, and certain amounts of CO_2 and NH_3 . The development of this impregnating procedure was an attempt to make the process more cost effective since all the impregnants can be added onto the carbon in one step. However, one drawback of this process is that the drying step in the impregnation has to be carried out at lower temperatures (about 120-150°C) to avoid self-ignition of the carbon. This may result in carbon which has moisture content higher than 2%.

Evaluation of the Amine-Impregnated Carbons

[0022] The amine-impregnated carbons prepared above were evaluated on its protection against toxic perfluoro-carbons, such as trifluoronitrosomethane. The impregnated carbons were loaded inside a container with an inside diameter of 10.5 cm, and to a bed height of 1.25 or 2 cm. A continuous flow of the test perfluorocarbon gas at 1000 mg/m^3 diluted inside an air stream at a flow rate of 30 L/min, 30°C and 80% RH was introduced into the carbon bed, and the effluent from the carbon bed was monitored for this perfluorocarbon gas, by a calibrated gas chromatography instrument. The breakthrough time is set at the time when the effluent perfluorocarbon gas concentration reaches 100 mg/m^3 , 1/10 of the original influent concentration.

[0023] Some selected amine-impregnated carbons were also tested and proven effective against other perfluoro-carbons such as perfluoroisobutene and hexafluoro-cyclobutene.

First Screening of Amine Impregnants

5 [0024] In order to evaluate all candidate amine impregnants systematically, the amine compounds used in this work were categorized into three major groups: aliphatic, aromatic and heterocyclic, which were then further divided into 3 classes: primary, secondary and tertiary, as shown in Table 1 below. In addition, an extra group under "Functional Substituents" was added to indicate amine compounds which contain additional substituents, such as a nitro group (as in 4-(4-nitrobenzyl)pyridine). Thus a simple 3x4 experiment matrix was set up so that any trend or anomaly could be correlated between the activity (protection against trifluoronitrosomethane) and the position in the matrix.

10 [0025] The amine impregnated carbons were evaluated as follows: beds of 125 or 170 mL impregnated carbon were loaded into a 10.5 cm diameter container, and tested against trifluoronitrosomethane at 1000 mg/m³ at an airflow of 30 L/min at 25°C and 80% RH. The breakthrough time results are collected in Table 2 below. The effluent from the canister was monitored for TFNM until a concentration of 100 mg/m³ was reached, and the time to reach this concentration from time zero was arbitrarily designated as the 'breakthrough time'. A typical challenge profile of TFNM through several of these amine-impregnated carbons is shown in Figure 1. Specifically, TFNM at 1000 mg/m³ on an activated carbon (125 mL, 10.5 cm diameter bed) impregnated with 7% (by weight) of triethylamine, that had been preconditioned at 80% RH

15 until constant weight was achieved.

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Primary	Aliphatic	Aromatic	Heterocyclic	Functional Substituents
	Diethylenetriamine $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ Ethylenediamine $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ Isopropylamine $\text{I}-\text{C}_3\text{H}_7\text{NH}_2$	Aniline <chem>Nc1ccccc1</chem> 4-phenylazobenzidine <chem>Nc1ccc(cc1)/N=N/c2ccc(N)cc2</chem> N,N-diethyl-1,4-phenylenediamine <chem>CCN(CC)c1ccc(N)cc1</chem>		Monoethanolamine OH NH_2 I CH_2-CH_2 Urea $\text{O}-\text{C}(\text{NH}_2)_2$ p-Toluenesulfonamide <chem>CS(=O)(=O)c1ccc(N)cc1</chem> o-Toluenesulfonamide
Secondary	Diisopropylamine $\text{I}-\text{C}_3\text{H}_7)_2\text{NH}$ Dipropylamine $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	Diphenylamine <chem>Nc1ccccc1-c2ccccc2</chem> Pyrrole <chem>c1cc[nH]1</chem>	Piperidine <chem>C1CCNCC1</chem>	
Tertiary	Triethylamine $(\text{C}_2\text{H}_5)_3\text{N}$ Triisobutylamine Trioctylamine	N,N-diethylaniline <chem>CCN(CC)c1ccccc1</chem> N,N-diethyl-1,4-phenylenediamine <chem>CCN(CC)c1ccc(N)cc1</chem> 4-phenylazobenzidine <chem>Nc1ccc(cc1)/N=N/c2ccc(N)cc2</chem>	Pyridine <chem>c1ccncc1</chem> 4-(4-nitrobenzyl)pyridine <chem>O=[N+]([O-])c1ccc(cc1)Cc2ccncc2</chem> Hexamethylenetetramine <chem>CN1CCCC1</chem> TEDA <chem>CN1CCCC1</chem>	4-(4-nitrobenzyl)pyridine <chem>O=[N+]([O-])c1ccc(cc1)Cc2ccncc2</chem>

[0026] It is noted that in Table 2 below, some secondary amines, such as diisopropylamine, pyrrole, and piperidine, and some tertiary amines such as triethylamine seemed to provide the best protection against TFNM. Impregnated carbons from these amines all produced longer breakthrough times than other amine impregnated carbons. Furthermore, it has been found from stoichiometry that 2 moles of TFNM were consumed per mole of secondary and tertiary amines. Thus it is expected that aliphatic secondary and tertiary amines to perform better against trifluoronitrosomethane than the rest of the candidate amines. Diamines did not appear to offer better protection against TFNM than other amines.

TABLE 2.

First Screening of Selected Amine Impregnants as Carbon
Carbon Impregnants for Enhanced Protection Against
Perfluorocarbons

Primary/Aliphatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Diethylenetriamine	6.0	29.5
Ethylenediamine	5.7	54.0
Isopropylamine	4.0	51.5

Primary/Aromatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Aniline	3.0	51.5
Aniline	6.0	52.5
Aniline	7.5	58.5
N,N-diethyl-1,4-phenylenediamine	3.3	36.0
4-phenylazoaniline	3.4	18.0

Secondary/Aliphatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Diisopropylamine	12.4	65.0
Diethylamine	7.1	45.3
Diethylenetriamine	6.0	29.5

TABLE 2.

First Screening of Selected Amine Impregnants
as Carbon Impregnants for Enhanced Protection
Against Perfluorocarbons* (continued)

Secondary/Aromatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Diphenylamine	5.5	6.3
Pyrrole	5.7	69.5

Secondary/Heterocyclic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Piperidine	3.6	65.0
Piperidine	5.5	71.0

Tertiary/Aliphatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Triethylamine	5.0	67.0

Tertiary/Aromatic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
N,N-diethylaniline	3.0	38.3
N,N-Diethyl-1,4-phenylenediamine	3.3	36.0
4-phenylazoaniline	3.4	18.0

TABLE 2.

First Screening of Selected Amine Impregnants
as Carbon Impregnants for Enhanced Protection
Against Perfluorocarbons* (continued)

Tertiary/Heterocyclic		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Pyridine	3.6	26.5
Pyridine	5.7	27.2
4-(4-Nitrobenzyl)- pyridine	5.8	34.5
Hexamethylenamine	6.5	42.8
Triethylenediamine	1.5	26.7

Functional Substituents		
Amine	% Loading (w/w)	Breakthrough Time (minutes)
Monoethanolamine	2.7	47.7
4-(4-Nitrobenzyl)- pyridine ⁽⁶⁾	5.8	34.5
Urea	3.1	54.0
Urea	2.0	56.5
N,N- dimethylformamide	7.0	43.5
O-toluenesulfonamide	5.0	68.5
P-toluenesulfonamide	5.0	39.7

*Note: All tests were carried out using 170 mL of the amine-impregnated carbon contained inside a filter canister body. All carbons were conditioned at 30°C and 80% RH until equilibrium weight of water was obtained before testing. Each challenge test consisted of a continuous flow of 1000 mg/m³ of CF₃NO in an air flow of 30 L/min at 80% RH and 30°C. The breakthrough time is determined as the time it takes the effluent test gas to reach 100 mg/m³.

Secondary Screening of Candidate Amines as Carbon Impregnants

[0027] In this section, the "better amine impregnants" were loaded onto the carbon at different loading levels and tested against trifluoronitrosomethane as shown in Table 3 below. The purpose is to identify the optimum loading level of the amines on the carbon.

[0028] In general, it appeared the higher the loading level of amines, the better the protection against TFNM. All the candidate amines shown in Table 3 showed very good performance. Furthermore, it seemed that dipropylamine, piperidine and triethylamine yielded the longest breakthrough times against TFNM at a loading level of 7% and pyrrole was even better at a loading level of 5%. Diisopropylamine seemed to be the best candidate amine because there was no penetration of TFNM at all loading levels. In all cases, the level of protection against TFNM improves, as the percentage loading level of amine increases.

TABLE 3

Second Screening: Protection Afforded by Selected Amine-Impregnated Dry Carbons Against TFNM			
Amine	% Loading	Density (g/mL)	Breakthrough Time (minutes)
Dipropylamine	4.0	0.62	71.5
	5.5	0.63	75.0
	7.2	0.65	85.0
	7.3	0.66	87.0
	12.0	0.68	83.0
Diisopropylamine	3.2	0.61	75.3
	5.1	0.62	79.1
	7.0	0.64	81.0
	9.9	0.67	78.4
Pyrrole	5.2	0.63	69.4
	6.8	0.64	74.0
Piperidine	3.3	0.61	65.0
	5.0	0.62	69.0
	6.9	0.64	72.0
	9.7	0.66	76.0
Triethylamine	3.5	0.61	39.7
	5.0	0.62	71.0
	6.8	0.63	75.0
	7.1	0.63	78.2
	8.1	0.64	81.5
	9.1	0.64	89.0
	15.0	0.70	87.2
Triisobutylamine	7.1	0.66	68.5
Trioctylamine	4.9	0.63	51.5
	7.2	0.65	47.7
Note: See footnote for Table 2 for test conditions.			

Third Screening of the Amine-Impregnated Carbons

[0029] Further testings were performed on other toxic perfluorocarbons such as perfluoroisobutene (PFIB) and hexafluorocyclobutene (HFCB) using triethylamine-impregnated carbon at 7% (w/w) loading level.

5 [0030] As seen in figures 2 and 3, the results were extremely promising. At a continuous challenge of 1000 mg/m³ of PFIB, the breakthrough time is 155 minutes (i.e. it takes 155 minutes for the PFIB effluent from the canister to reach 100 mg/m³). The breakthrough time for tris(trifluoromethyl)methane (TRIS), a non-toxic breakdown product from the reaction between the activated carbon and PFIB is 163.2 minutes. For HFCB, the breakthrough time is 28.8 minutes under similar conditions. More specifically, in both figures 2 and 3, an activated carbon (125 mL, 10.5 cm diameter bed) impregnated with 7% (by weight) of triethylamine, that had been preconditioned at 80% RH until constant weight was achieved, is involved; (note that in figure 2, perfluoroisobutene (labelled PFIB) converts to form tris(trifluoromethyl)methane (labelled TRIS).

10 [0031] To investigate the universality of this amine impregnation process, other activated carbons, namely the BPL (carbon with no previous impregnation history) and ASC/TEDA carbon were studied. The acceptance of amine impregnants on these carbons, and the protection against trifluoronitrosomethane and other perfluorocarbons were evaluated. The methods for loading the amine impregnants on these carbons are similar to those described above for the ASC whetstone. The results are summarized in Table 4. As shown, the choice of base carbons make very little effect on the performance of the impregnated carbon against TFNM.

TABLE 4

Protection Against Trifluoronitrosomethane by Using Different Base Carbons		
Base Carbon	Impregnants	Breakthrough Time (minutes)
BPL	Dipropylamine	72.8
	Triethylamine	73.0
	Piperidine	72.0
ASC/T	Dipropylamine	79.0
	Triethylamine	82.0
	Piperidine	72.8
Notes: (1) All amine impregnants were loaded at 5% by weight. (2) All challenge tests were conducted using the same conditions as in Table 2.		

40 [0032] Similar experiments using ASC/TEDA carbons (i.e. without the amine impregnants mentioned in this disclosure) result in breakthrough times much lower than those shown in figures 1 to 3, depending on the perfluorocarbon.

45 **Claims**

1. A breathing gas filter composition providing protection against toxic perfluorocarbons, comprising substantially dry activated carbon and an organic amine impregnant in an amount of 1.5 to 18% by weight, based on the weight of the carbon, characterised in that the composition additionally comprises 0.1 to 10% by weight, based on the weight of the carbon, of an alkaline hydroxide.
2. A composition according to claim 1, wherein the organic amine is included in an amount of 4 to 7% by weight, based on the weight of the carbon.
- 55 3. A composition according to claim 1 or claim 2, wherein the organic amine is selected from the group consisting of substituted amines, amides and sulfonamides.
4. A composition according to claim 1 or claim 2, wherein the organic amine is selected from the group consisting of

aliphatic secondary and tertiary amines.

- 5 5. A composition according to claim 1 or claim 2 wherein the organic amine is selected from the group consisting of ethylenediamine, dipropylamine, isopropylamine, aniline, N,N-diethyl-1,4-phenyl nediamine, 4-phenylazoaniline, diisopropylamine, diethylamine, diethylenetriamine, diphenylamine, pyrrole, piperidine, triethylamine, triisobutylamine, trioctylamine, N,N-diethylaniline, 4-(4-nitrobenzyl)-pyridine, hexamethylenamine, monoethanolamine, urea, N,N-dimethylformamide, o-toluenesulfonamide and p-toluenesulfonamide.
- 10 6. A process for impregnating activated carbon by placing a low vapour pressure organic amine in contact with substantially dry activated carbon, characterised by the steps of subjecting the carbon and amine to positive pressure of 1-5 Pa in an oxygen-free inert gas atmosphere and then heating the carbon and amine for an extended period while maintaining the positive pressure of 1-5 Pa in an oxygen-free inert gas atmosphere, and pre-treating the activated carbon with a compound selected from the group consisting of an alkaline hydroxide in an amount of 0.1 to 10% by weight, based on the weight of the carbon, a suitable halogen and a suitable halide salt.
- 15 7. A process according to claim 6, including the additional step of storing the amine-impregnated carbon in an oxidizer-free enclosure.
- 20 8. A process according to claim 6 or claim 7, wherein the heating step is effected at 40° to 60° C. for 1 to 72 hours.
9. A process according to any one of claims 6 to 8, wherein the oxygen-free inert gas is selected from the group consisting of nitrogen, argon and helium.
- 25 10. A process according to any one of claims 6 to 9, wherein the amine is selected from the group consisting of aliphatic secondary and tertiary amines.
11. A process according to any one of claims 6 to 11, wherein the amine is included in an amount of 4 to 7% by weight, based on the weight of the carbon.
- 30 12. A process according to any one of claims 6 to 11 wherein the activated carbon is selected from the group consisting of carbon impregnated with copper, silver and chromium, unimpregnated base carbon, and carbon impregnated with copper, silver, chromium and triethylenediamine.
- 35 13. A process according to any one of claims 6 to 12, wherein the amine is selected from dipropylamine and triethylamine.
- 40 14. A process for impregnating activated carbon with a solid amine compound, comprising dissolving the amine in a solvent selected from water and organic solvents and adding the amine solution to the activated carbon characterised by the step of pre-treating the activated carbon with a compound selected from the group consisting of an alkaline hydroxide in an amount of 0.1 to 10% by weight, based on the weight of carbon, a suitable halogen and a suitable halide salt.

Patentansprüche

- 45 1. Atemgasfilterzusammensetzung, die Schutz gegen toxische Perfluorkohlenstoffe bietet, die im wesentlichen trockene Aktivkohle und ein organisches Amin-Imprägnierungsmittel in einem Anteil von 1,5 bis 18 Gew.-%, bezogen auf das Gewicht der Kohle, umfaßt, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich 0,1 bis 10 Gew.-%, bezogen auf das Gewicht der Kohle, eines Alkalihydroxids aufweist.
- 50 2. Zusammensetzung nach Anspruch 1, wobei das organische Amin in einem Anteil von 4 bis 7 Gew.-%, bezogen auf das Gewicht der Kohle, enthalten ist.
3. Zusammensetzung nach Anspruch 1 oder Anspruch 2, wobei das organische Amin aus der Gruppe ausgewählt ist, die aus substituierten Aminen, Amiden und Sulfonamiden besteht.
- 55 4. Zusammensetzung nach Anspruch 1 oder Anspruch 2, wobei das organische Amin aus der Gruppe ausgewählt ist, die aus aliphatischen sekundären und tertiären Aminen besteht.

5. Zusammensetzung nach Anspruch 1 oder Anspruch 2, wobei das organische Amin aus der Gruppe ausgewählt ist, die aus Ethylendiamin, Dipropylamin, Isopropylamin, Anilin, N,N-Diethyl-1,4-phenylendiamin, 4-Phenylazoanilin, Diisopropylamin, Diethylamin, Diethylentriamin, Diphenylamin, Pyrrol, Piperidin, Triethylamin, Triisobutylamin, Tri-octylamin, N,N-Diethylanilin, 4-(4-Nitrobenzyl)-pyridin, Hexamethylenamin, Monoethanolamin, Harnstoff, N,N-Dimethylformamid, o-Toluolsulfonamid und p-Toluolsulfonamid besteht.
6. Verfahren zum Imprägnieren von Aktivkohle durch Inkontaktbringen eines organischen Amins mit niedrigem Dampfdruck mit im wesentlichen trockener Aktivkohle, gekennzeichnet durch die folgenden Schritte: Anwenden eines Überdrucks von 1-5 Pa auf die Kohle und das Amin in einer sauerstofffreien Inertgas-Atmosphäre und anschließendes Erhitzen der Kohle und des Amins über längere Zeit unter Beibehaltung des Überdrucks von 1-5 Pa in einer sauerstofffreien Inertgas-Atmosphäre und Vorbehandeln der Aktivkohle mit einer Verbindung, ausgewählt aus der Gruppe, die besteht aus einem Alkalihydroxid in einem Anteil von 0,1 bis 10 Gew.-%, bezogen auf das Gewicht der Kohle, einem geeigneten Halogen und einem geeigneten Halogenidsalz.
7. Verfahren nach Anspruch 6, das den zusätzlichen Schritt Lagern der aminimprägnierten Kohle in einer oxidationsmittelfreien Hülle aufweist.
8. Verfahren nach Anspruch 6 oder Anspruch 7, wobei der Erhitzungsschritt bei 40° bis 60°C über 1 bis 72 Stunden ausgeführt wird.
9. Verfahren nach einem der Ansprüche 6 bis 8, wobei das sauerstofffreie Inertgas aus der Gruppe ausgewählt ist, die aus Stickstoff, Argon und Helium besteht.
10. Verfahren nach einem der Ansprüche 6 bis 9, wobei das Amin aus der Gruppe ausgewählt ist, die aus aliphatischen sekundären und tertiären Aminen besteht.
11. Verfahren nach einem der Ansprüche 6 bis 11, wobei das Amin in einem Anteil von 4 bis 7 Gew.-%, bezogen auf das Gewicht der Kohle, enthalten ist.
12. Verfahren nach einem der Ansprüche 6 bis 11, wobei die Aktivkohle aus der Gruppe ausgewählt ist, die aus mit Kupfer, Silber und Chrom imprägnierter Kohle, nicht imprägnierter Basiskohle und mit Kupfer, Silber, Chrom und Triethylendiamin imprägnierter Kohle besteht.
13. Verfahren nach einem der Ansprüche 6 bis 12, wobei das Amin aus Dipropylamin und Triethylamin ausgewählt ist.
14. Verfahren zum Imprägnieren von Aktivkohle mit einer festen Aminverbindung, das die Schritte Auflösen des Amins in einem Lösungsmittel, das aus Wasser und organischen Lösungsmitteln ausgewählt ist, und Zugabe der Aminlösung zur Aktivkohle umfaßt, gekennzeichnet durch den Schritt Vorbehandeln der Aktivkohle mit einer Verbindung, die aus der Gruppe ausgewählt ist, die besteht aus einem Alkalihydroxid in einem Anteil von 0,1 bis 10 Gew.-%, bezogen auf das Gewicht der Kohle, einem geeigneten Halogen und einem geeigneten Halogenidsalz.

Revendications

1. Composition de filtration du gaz de respiration comportant une protection contre les perfluorocarbones toxiques, comprenant du carbone activé essentiellement sec et un imprégnant d'amine organique en une quantité de 1,5 à 18% en poids, par rapport au poids du carbone, caractérisée en ce que la composition comprend de plus 0,1 à 10% en poids, par rapport au poids du carbone, d'un hydroxyde alcalin.
2. Composition suivant la revendication 1, dans laquelle l'amine organique est incorporée en une quantité de 4 à 7% en poids, par rapport au poids du carbone.
3. Composition suivant l'une ou l'autre des revendications 1 et 2, dans laquelle l'amine organique est choisie dans le groupe comprenant les amines, amides et sulfonamides substitués.
4. Composition suivant l'une ou l'autre des revendications 1 et 2, dans laquelle l'amine organique est choisie dans le groupe comprenant les amines secondaires et tertiaires aliphatiques.
5. Composition suivant l'une ou l'autre des revendications 1 et 2, dans laquelle l'amine organique est choisie dans le

groupe comprenant l'éthylènediamine, la dipropylamine, l'isopropylamine, l'aniline, la N,N-diéthyl-1,4-phénylènediamine, la 4-phénylazoaniline, la diisopropylamine, la diéthylamine, la diéthylènetriamine, la diphénylamin , le pyrrole, la pipéridin , la triéthylamine, la triisobutylamine, la tricotylamine, la N,N-diéthylanilin , la 4-(4-nitrobenzyl)pyridine, l'hexaméthylèneamine, la monoéthanolamine, l'urée, le N,N-diméthylformamide, l'o-toluènesulfonamide et le p-toluènesulfonamid .

- 5 6. Procédé d'imprégnation de carbone activé en plaçant une amine organique à faible pression de vapeur en contact avec du carbone activé essentiellement sec, caractérisé par les étapes qui consistent à soumettre le carbone et l'amine à une pression positive de 1-5 Pa dans une atmosphère de gaz inerte exempte d'oxygène et ensuite à chauffer le carbone et l'amine pendant une période prolongée tout en maintenant la pression positive de 1-5 Pa dans une atmosphère de gaz inerte exempte d'oxygène, et à prétraiter le carbone activé avec un composé choisi dans le groupe comprenant un hydroxyde alcalin en une quantité de 0,1 à 10% en poids, par rapport au poids du carbone, un halogène approprié et un sel d'halogénure approprié.
- 10 7. Procédé suivant la revendication 6, comprenant l'étape additionnelle de conserver le carbone imprégné d'amine dans une enceinte exempte d'oxydant.
- 15 8. Procédé suivant l'une ou l'autre des revendications 6 et 7, dans lequel l'étape de chauffage est effectuée à une température de 40° à 60°C pendant 1 à 72 heures.
- 20 9. Procédé suivant l'une quelconque des revendications 6 à 8, dans lequel le gaz inerte exempt d'oxygène est choisi dans le groupe comprenant l'azote, l'argon et l'hélium.
- 25 10. Procédé suivant l'une quelconque des revendications 6 à 9, dans lequel l'amine est choisie dans le groupe comprenant les amines secondaires et tertiaires aliphatiques.
- 30 11. Procédé suivant l'une quelconque des revendications 6 à 11, dans lequel l'amine est incorporée en une quantité de 4 à 7% en poids, par rapport au poids du carbone.
- 35 12. Procédé suivant l'une quelconque des revendications 6 à 11, dans lequel le carbone activé est choisi dans le groupe comprenant un carbone imprégné de cuivre, d'argent et de chrome, un carbone de base non imprégné et un carbone imprégné de cuivre, d'argent, de chrome et de triéthylènediamine.
- 40 13. Procédé suivant l'une quelconque des revendications 6 à 12, dans lequel l'amine est choisie parmi la dipropylamine et la triéthylamine.
- 45 14. Procédé d'imprégnation de carbone activé avec un composé d'amine solide, comprenant la dissolution de l'amine dans un solvant choisi parmi l'eau et les solvants organiques et l'addition de la solution d'amine au carbone activé, caractérisé par l'étape de prétraitement du carbone activé avec un composé choisi dans le groupe comprenant un hydroxyde alcalin en une quantité de 0,1 à 10% en poids, par rapport au poids de carbone, un halogène approprié et un sel d'halogénure approprié.
- 50
- 55

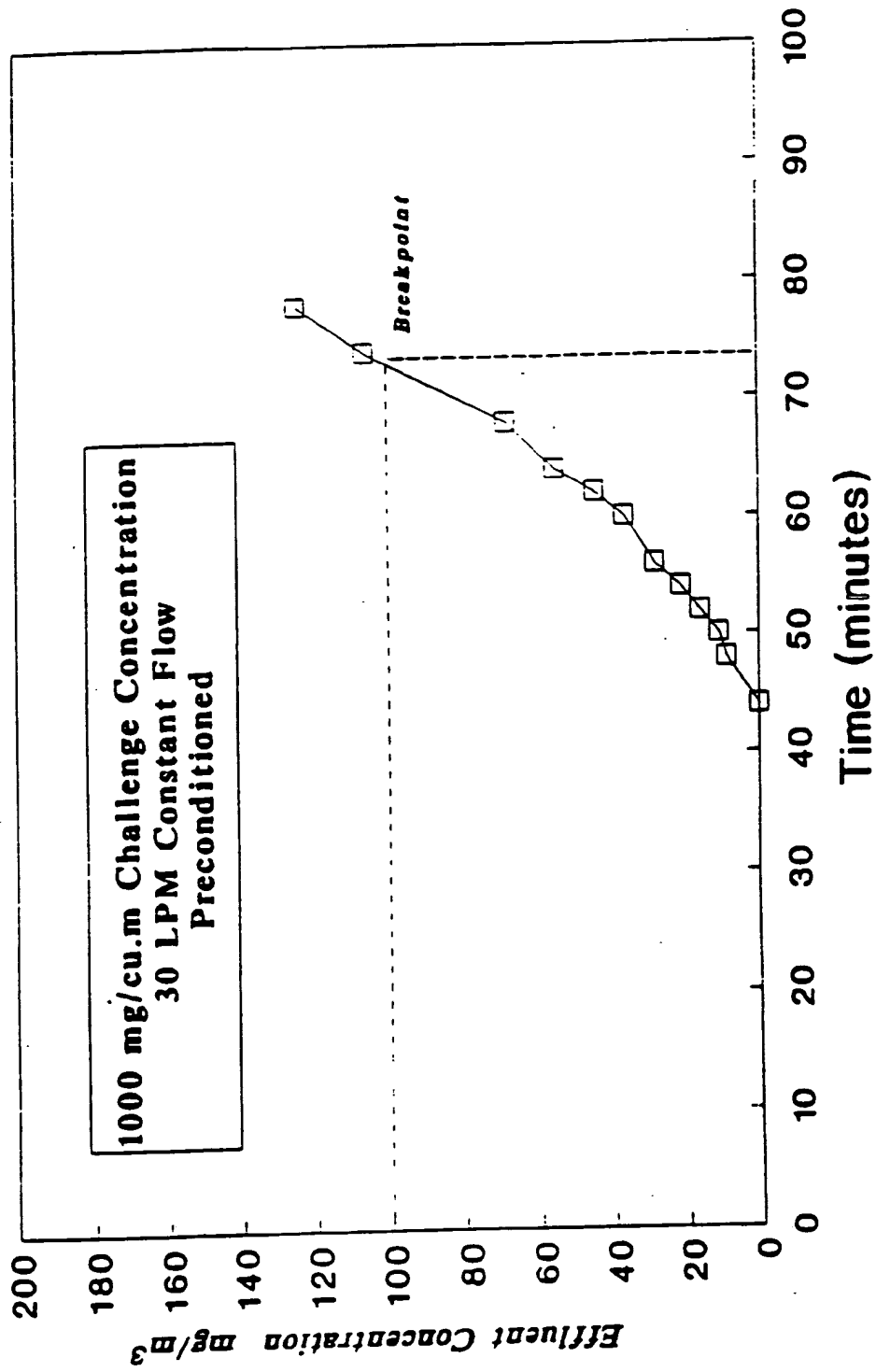


FIG. 1

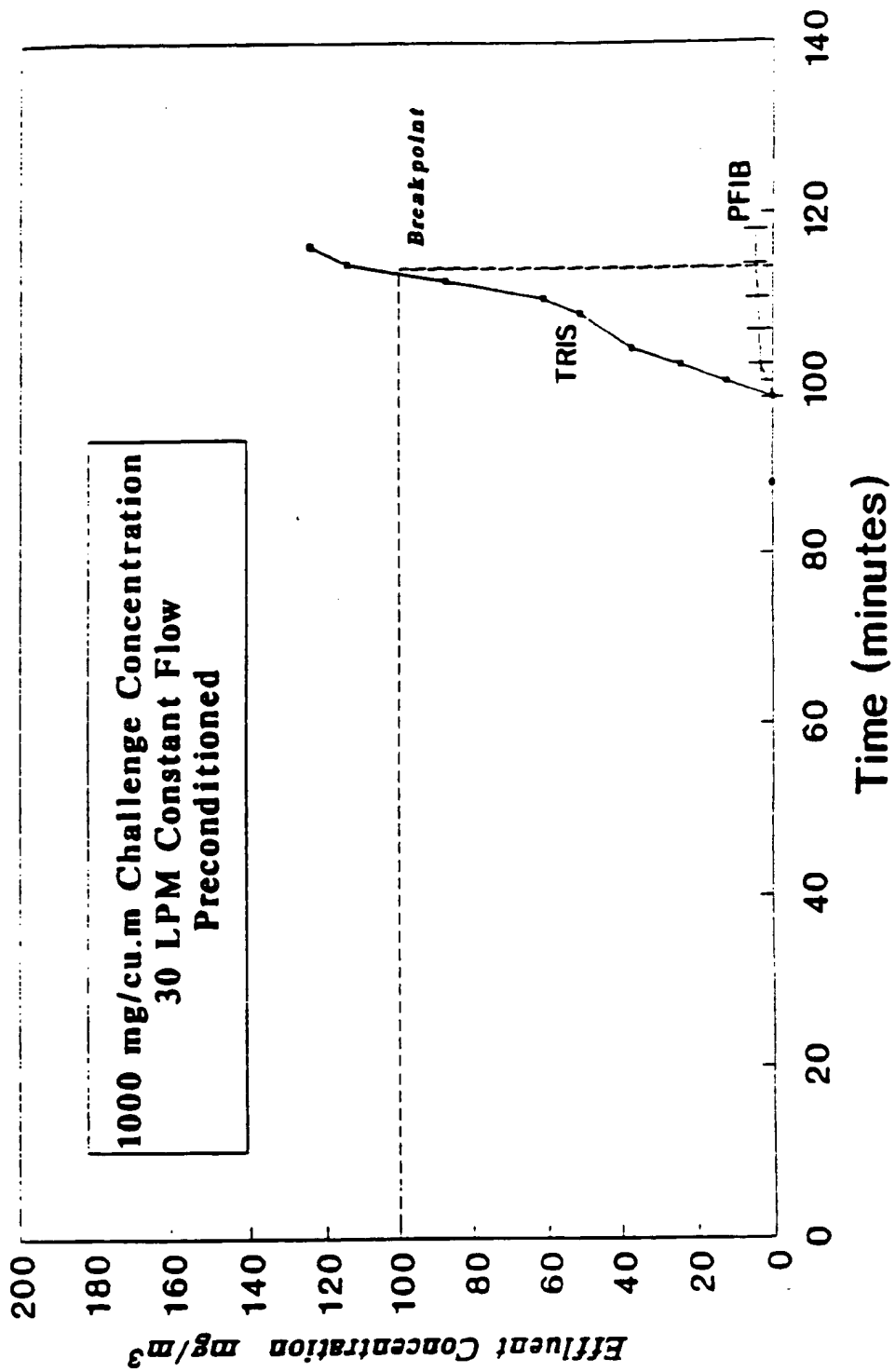


FIG. 2

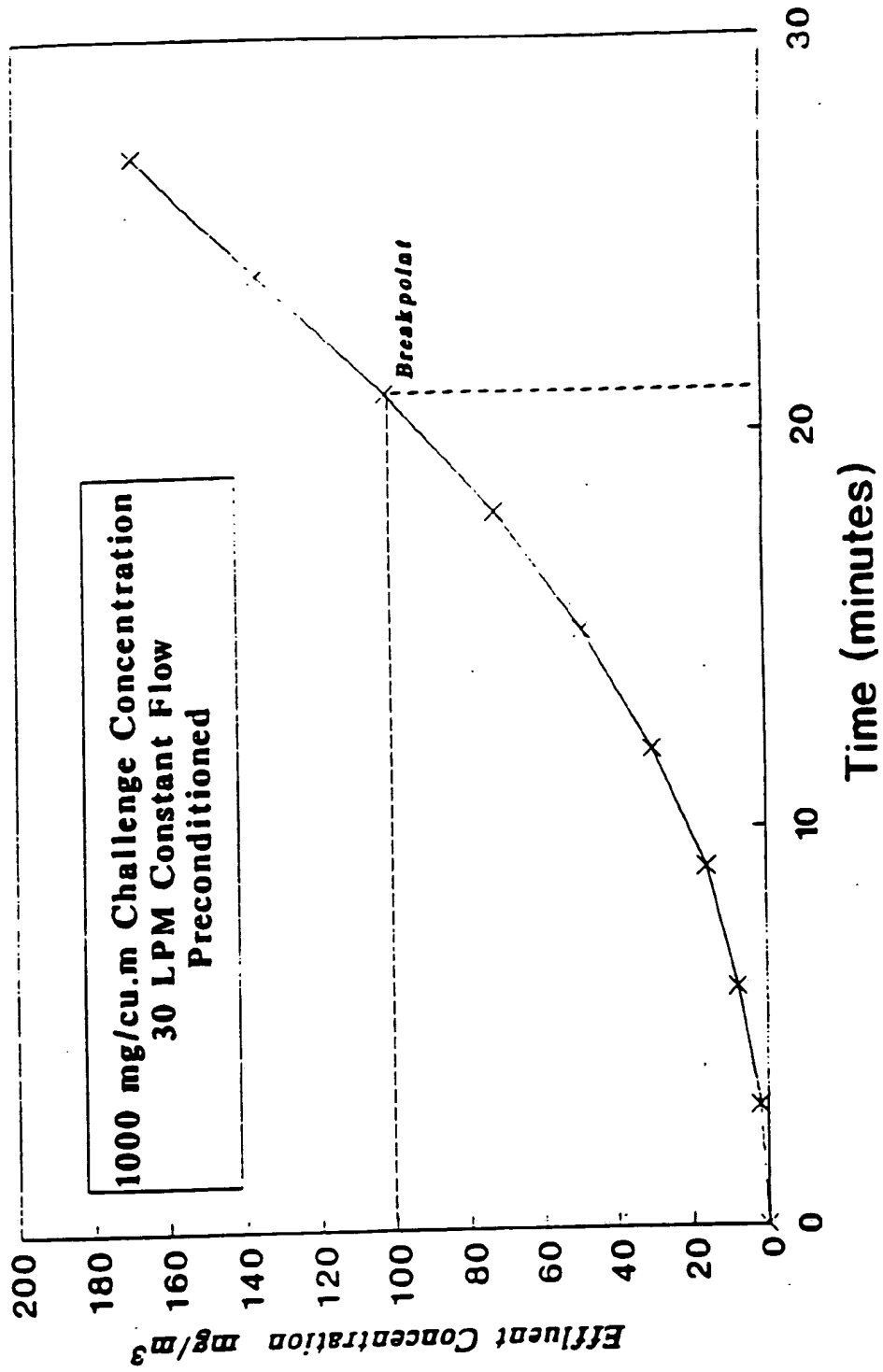


FIG. 3

